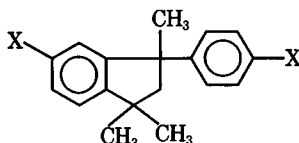


**Polyamides and Polyesters Derived from 1,1,3-Trimethyl-3-(*p*-aminophenyl)-5-indanamine and 1,1,3-Trimethyl-3-(*p*-hydroxyphenyl)-5-indanol**

Previous studies have shown that aromatic polyesters derived from 1,1,3-trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan (I) exhibit high glass transition temperatures (above 200°C).<sup>1</sup> It was therefore of interest to study the thermal properties of polymers prepared from other derivatives of 1,1,3-trimethyl-3-phenylindan.

In the present study, polyamides of 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine (II) and polyesters of 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III) were prepared and found to have high glass transition temperatures as well. A substantial increase in the glass transition temperature occurs when the ester linkage is replaced by the amide moiety.



X = -CO<sub>2</sub>H (I)

X = -NH<sub>2</sub> (II)

X = -OH (III)

#### EXPERIMENTAL

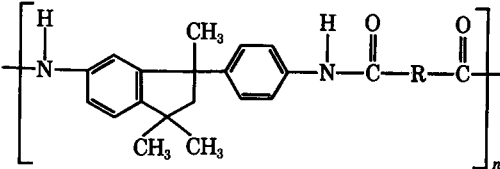


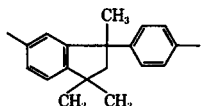
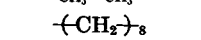
The melting point is uncorrected. The infrared spectrum was recorded with a Perkin-Elmer 237B grating infrared spectrophotometer. NMR spectrum was obtained with a Varian A60 instrument with tetramethylsilane as internal standard. The mass spectrum was obtained with a Hitachi Perkin-Elmer RMS-4 mass spectrometer. X-ray diffraction patterns were measured with an XRD-3 diffractometer. Glass transition temperatures were determined with DuPont 900 and 990 differential scanning calorimeters at a heating rate of 10°C/min in nitrogen. Unless otherwise indicated, glass transition temperatures were second heating values determined at the recovery point. Thermogravimetric analyses were determined with a DuPont 950 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen. Inherent viscosities were measured with 1:1 (wt) phenol:chlorobenzene at a concentration of 0.25 g of polymer in 100 ml of solution at 25°C.

#### Materials

1,1,3-Trimethyl-3-(*p*-aminophenyl)-5-indanamine (II) was prepared by the method of Petropoulos and Fisher<sup>2</sup> from 1,1,3-trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan (I). 1,1,3-Trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III) was prepared from II as follows:

To a solution of 24.5 g of concentrated sulfuric acid in 100 ml of water was added 16.45 g (0.062 mole) of 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine (II) and 100 ml of water. This solution was cooled to approximately 4°C and a solution of 9.0 g (0.13 mole) of sodium nitrite in 17.5 ml of water was added over 20 min, the reaction temperature being maintained below 12°C. On completion of this addition, cooling was discontinued and the mixture was stirred at room temperature for approximately 65 hr. At this time, the aqueous phase was decanted and the solids were washed well with water and heated in 250 ml of refluxing benzene for 1 hr with removal of the azeotropic distillate. The volume of benzene removed was replaced, and the solution was treated with decolorizing carbon, filtered through diatomaceous earth, concentrated to one half volume, and allowed to cool with seeding. After crystallizing overnight, the solids were collected, washed with hexane, and dried. A second recrystallization from benzene

TABLE I  
Properties of Polyamides Derived from 1,1,3-Trimethyl-3-(*p*-aminophenyl)-5-indanamine

			
R	Inherent viscosity, dl/g	<i>T</i> <sub>g</sub> , °C	TGA onset of weight loss, °C
	0.89	352	391
	0.41	327 <sup>a</sup>	357
	1.01	341	400
	0.37	175	295

<sup>a</sup> First heating.

yielded 1.6 g (9.6%) of 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III); mp 191.5–193.0°C (reported<sup>2</sup> mp 165–166°C). The melting point of this material was similar to that of material (mp 189.0–190.5°C) previously prepared by this method which gave the following analyses.

ANAL. Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>: C, 80.56%; H, 7.51%. Found: C, 80.5%; H, 7.5%.

Infrared (KBr) bands were observed at 845, 1225, 1510, 2950, and 3400 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub> + D<sub>2</sub>O) showed  $\tau$  2.56–3.50 (*m*, 3.54, aromatic), 7.77 (*d*, 1.00, *J* = 5 Hz, >CH<sub>2</sub>), 8.40 (*s*, 1.50, 3 -CH<sub>3</sub>), 8.71 (*s*, 1.54, geminal CH<sub>3</sub>), and 8.98 (*s*, 1.50, geminal CH<sub>3</sub>); mass spectrum *m/e* 268, 253, 159, 119, and 78.

1,1,3-Trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan dichloride was prepared as described by Hamb.<sup>1</sup> 4,4'-Isopropylidenediphenol bischloroformate was prepared by the method of Schnell and Bottenbruch.<sup>4</sup> Terephthaloyl chloride and isophthaloyl chloride were purified by the procedure of Sorenson and Campbell.<sup>5</sup> All other chemicals were available commercially.

### Polymers

Polyamides were prepared as described by Morgan.<sup>6</sup> An example is the following.

In a Waring Blendor was placed a solution of 2.66 g (0.01 mole) of 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine (II) in 56 ml of tetrahydrofuran and a solution of 2.12 g (0.02 mole) of sodium carbonate in 67 ml of distilled water. To this stirred mixture was added a solution of 2.03 g (0.01 mole) of terephthaloyl chloride in 17 ml of tetrahydrofuran. This mixture was stirred for 10 min and poured into methanol. The polymer

was isolated, washed with methanol, and dried *in vacuo* at 80°C for 5 hr. The inherent viscosity of the polymer was determined to be 0.89.

Polyesters were prepared interfacially in a manner similar to that described in Sorenson.<sup>7</sup> An example of this procedure follows.

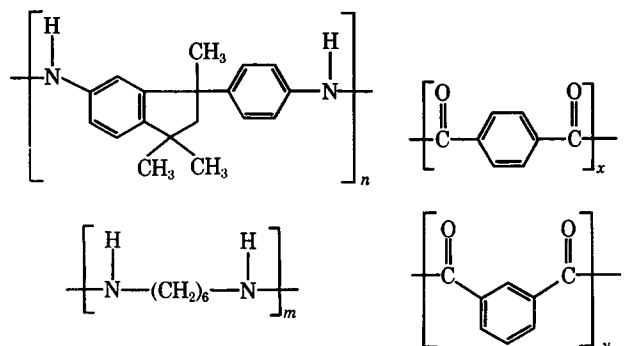
To a mixture of 1.342 g (0.005 mole) of 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III), 22 ml (0.011 mole) of 0.5*N* sodium hydroxide, 10 ml of distilled water, and 1 drop of tri-*n*-butylamine in a Waring Blendor was added a solution of 1.015 g (0.005 mole) of terephthaloyl chloride in 25 ml of methylene chloride. The mixture was stirred for 8 min while the sides of the Blendor jar were rinsed with water. Polymer precipitated during this time. Methanol was added to the mixture to fully precipitate the polymer. The methanol was decanted, and the polymer was washed again with methanol, collected, and dried. The inherent viscosity was 0.44.

## RESULTS AND DISCUSSION

Properties of polyamides and copolyamides of 1,1,3-trimethyl-3-(*p*-aminophenyl)-5-indanamine (II) are given in Tables I and II. Inherent viscosities range from 0.37 to 1.01 and represent polymers formed generally within 10 min of reaction time.

The glass transition temperatures are extremely high and have been rationalized as due to the stiffness and bulk of the phenylindan moiety and the hydrogen bonding of the amide linkage. The bulkiness of the phenylindan moiety can also be shown to affect the morphology of the homopolyamides. No polymer melting temperatures were ever observed, and the x-ray diffraction spectra show no crystalline content. The absence of crystal structure in these highly polar polymers is apparently the result of poor packing quality due to the bulkiness of the phenylindan moiety. The hydrogen-bonding contribution to the glass transition temperatures was determined by comparison of this property with that of polyesters derived from 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III). Properties of these polyesters are given in Table III. The terephthalamide and sebacamide polymers have glass transition temperatures higher than the

TABLE II  
Properties of Copolyamides Derived from 1,1,3-Trimethyl-3-(*p*-aminophenyl)-5-indanamine

						
<i>n</i>	<i>m</i>	<i>x</i>	<i>y</i>	Inherent viscosity, dl/g	<i>T<sub>g</sub></i> , °C	TGA onset of weight loss, °C
100	0	50	50	0.83	297	391
50	50	100	0	0.82	272*	340

\* First heating.

TABLE III

Properties of Polyesters Derived from 1,1,3-Trimethyl-3-(*p*-hydroxyphenyl)-5-indanol

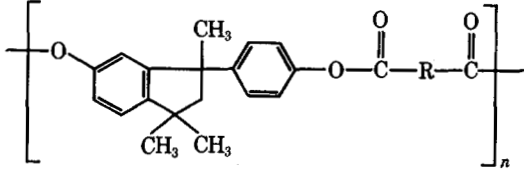

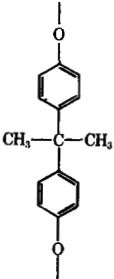
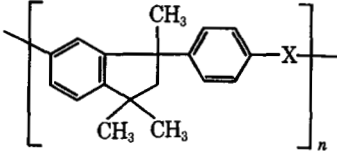
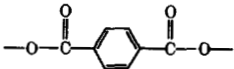
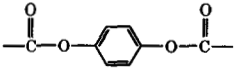
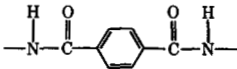
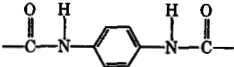
		
R	Inherent viscosity, dl/g	<i>T<sub>g</sub></i> , °C
	0.44	272
	0.33	89
$-(CH_2)_8-$	0.20	41

TABLE IV

Properties of Polymers Containing 1,1,3-Trimethyl-3-phenylindan-4',5-diyl and *p*-Phenylene Moieties

		
X	Inherent viscosity, dl/g	<i>T<sub>g</sub></i> , °C
	0.44	272
	0.25	258 <sup>a</sup>
	0.89	352
	0.93	372 <sup>b</sup>

<sup>a</sup> Prepared in the melt phase from I and *p*-phenylene diacetate.<sup>b</sup> Prepared interfacially from I diacid chloride and *p*-phenylenediamine.

TABLE V

Properties of Copolyesters Derived from 1,1,3-Trimethyl-3-(*p*-hydroxyphenyl)-5-indanol and 1,1,3-Trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan

<i>n</i>	<i>m</i>	<i>x</i>	<i>y</i>	Inherent viscosity, dl/g	<i>T<sub>g</sub></i> , °C
50	50	0	100	0.72	244 <sup>a</sup>
0	100	50	50	0.58	262

<sup>a</sup> Prepared interfacially from I diacid chloride, terephthaloyl chloride, and 4,4'-isopropylidenediphenol.

terephthalate and sebacate polymers by 80°C and 134°C, respectively. Since the corresponding polyamides and polyesters are considered equally bulky and stiff, the glass transition temperature difference is visualized to be a function of the hydrogen bonding. Taking this correlation one step further, we compared the terephthalamide and terephthalate polymers with the polyamide of 1,1,3-trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan (I) and *p*-phenylenediamine and the polyester of 1,1,3-trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan (I) and hydroquinone. Some properties of these polymers are listed in Table IV. It is seen that the bonding arrangement of the ester or amide functional group has little effect on the glass transition temperature. However, when the ester moiety is replaced by the amide function, the resultant increase in hydrogen bonding produces an average increase in the glass transition temperature of approximately 100°C.

Table V compares the glass transition temperature of the copolyester of 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (III) (50 mole-% in feed), 4,4'-isopropylidenediphenyl (50 mole percent in feed), and terephthaloyl chloride and the copolyester of 1,1,3-trimethyl-3-(*p*-carboxyphenyl)-5-carboxyindan dichloride (50 mole-% in feed), terephthaloyl chloride (50 mole-% in feed) and 4,4'-isopropylidenediphenol. The glass transition temperatures can be seen to be of nearly equal value.

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#### References

1. F. L. Hamb, U.S. Pat. 3,634,089 (1972).
2. J. C. Petropoulos and J. J. Fisher, *J. Amer. Chem. Soc.*, **80**, 1938 (1958).
3. J. C. Petropoulos and F. A. Sullivan, U.S. Pat. 2,979,534 (1961).
4. H. Schnell and L. Bottenbruch, *Makromol. Chem.*, **57**, 1 (1962).

5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 84.
6. P. W. Morgan, in *Condensation Polymers: By Interfacial and Solution Methods*, Interscience, New York, 1965, p. 492.
7. W. R. Sorenson, in *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 119.

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